

CORROSION AND ELECTROCHEMICAL RESEARCHES

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Abstract

We wish to introduce the work of the research group for corrosion and electrochemistry of Institute of Inorganic Chemistry, Technical University of Budapest. The main fields of our investigations were the electrogalvanizing of palladium-nickel alloy-coatings, the study of the sealing of the anodic oxide-layers, the corrosion-resistance of titanium-carbide steel-alloys, the effectiveness of inhibitors protecting the steel reinforcement of cellular concrete and the study of the corrosion effect of chemical agents used for salting winter roads.

Keywords: corrosion, layers, inhibitors, salting.

Introduction

The corrosion and electrochemical researches started here more than 40 years ago. Even under the leadership of Prof. PROSZT some electrochemical studies were done here and it was the starting point of the study of the surface conditions of metals as well. At first the investigations covered primarily the area of metals and alloys, later they focused on different layers and corrosion inhibitors. On the field of the layers among others the following materials were studied in our Institute: metallized aluminum and zinc-aluminum alloy-layers [1, 2], phosphate-layers [3, 4], silicone-resin-based layers [5, 6], galvanic layers [7-10], chromate layers [11, 12], under-spraying compounds [13]. In the territory of inhibitor study among others the following compounds were investigated: mercaptanes and amines [14], silatranes [15], intermediates of rubber industry [16], surface-active materials [17], organic nitrogen-compounds [18]. We would like to introduce some of our results found recently.

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Palladium-nickel Alloy-layer

Galvanic selection of wear- and corrosion-resistant palladium-nickel alloy-layers was studied [19]. This layer has favourable properties and it is suitable for the substitution of hard gold used in electronic- and jeweller's trade. The goal of our work was to optimize the operation parameters of the galvanic-electrolytic addition system of palladium-nickel developed and still in progress at General Design Institute for the Engineering Industry. This electrolyte consisted of moistener and 3 different polishing additives.

Phosphoric acid derivatives as moistener [A] and sulfamide derivatives as primary polisher [B] were applied. Secondary polishers [C, D] were pyridine derivatives. The electrolytes of the following compounds were used for the experiment:

[Pd(NH ₃) ₆]Cl ₂	10g/dm ³
[Ni(NH ₃) ₆]SO ₄	10g/dm ³
(NH ₄) ₂ SO ₄	75g/dm ³
A component	0.1g/dm ³
B component	2.0g/dm ³
C component	0.04 – 0.16g/dm ³
D component	0.8g/dm ³

The effect of the additives on the cathodic metal separation was studied with the help of potentiodynamic curves. On the effect of the additives the speed of metal separation decreased and the polarization curves shifted to negative direction. It was found that the moistener and the different polishing components cause cathodic polarization of different size. The biggest cathodic polarization (cca. 100 mV) occurred in the presence of 'C' polishing additive.

Further on, as a function of 'C' component the composition of the layer and its physical and corrosion properties were studied. The optimal concentration of 'C' polishing additive was determined: 0.08g/dm³. Finally, besides the optimal electrolytic solution-compound, the effect of the mixture of the solution and cathodic electric density on the properties of the obtained layer were observed.

In case of mixing the solution, the Pd-contents of the layer grows by the increase of the electric density. The parameters of the metal separation — as diffusion-controlled processes are in question — can be better checked. The desired 75% Pd-concentration can be achieved at 0.8A/dm² electric density and under such circumstances other properties of the layer also meet the requirements.

The optimal galvano-electric compound and the layer produced with optimal operation parameters seem suitable for the substitution of hard gold used in industry.

Anodic Oxide Layer

The structure and properties of anodic oxide layer, which was obtained on aluminum with an electrochemical method, were investigated as a function of the temperature of anodic process [20]. Furnace-aluminum plate with the purity of 99.5 % was used for the experiments. The anodic oxidation was carried out in $180\text{g}/\text{dm}^3\text{H}_2\text{SO}_4$ solution containing $3\text{g}/\text{dm}^3$ solute aluminum with direct current at cell tension of 16 V.

The temperature of the electrolyte was changed by 2°C between 10 and 20°C . In each case $15\ \mu\text{m}$ thick top layer was formed, which needed 60 ($18\text{--}20^\circ\text{C}$), 90 ($14\text{--}16^\circ\text{C}$) and 120 minutes ($10\text{--}12^\circ\text{C}$). The oxide layer was tightened in distilled water at 100°C .

The morphology, solidity, wear-resistance and corrosion properties of untight and tight top layers formed at different temperatures were studied.

Transmission-scanning electron microscopic photos provided information about the morphology of the layers. Sealing was determined in solutions containing H_3PO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ on the basis of solubility (weight loss) and admittance measures. Corrosion-resistance investigations were carried out in NaCl -, CH_3COOH - and H_2O_2 solutions. It was found that by decreasing the temperature of anodic oxidation the hardness of the layer would grow, at the same time, as a result of sealing the hardness of the top layer would decrease approximately with 40–60 HV. The hardest ones (440 and 510 HV) are the tight and untight layers produced at 10°C , which belong to the so-called 'hard oxide layers'. The temperature increased by 10°C will result in more than double hardness decrease.

The temperature-dependence of wear-resistance shows a tendency similar to that of hardness. The sealing and corrosion-resistance of the layers improve by cooling. All the above-mentioned data show that the structure of the top-layer considerably changes under 14°C . The layer becomes tighter, harder, its mechanical and corrosion properties improve, it is less suitable for post-colouring.

Titaniumcarbide-steel Alloys

In different medium the corrosion-resistance of titaniumcarbide-steel alloys produced in a powder metallurgical way was studied in co-operation with the Technical University of Tallinn [21] gravimetric, metallographical and electrochemical investigations were carried out.

The samples investigated were different in TiC contents (50 and 60 %) and in the way they were produced. The corrosion-resistance did not depend on the way of production, the bending strength and impact energy,

however, showed higher values at samples synthetically created of their elements.

The TiC-Fe-Ni-Cr alloys studied in 20% NaOH solution are completely resistant up to 80%. The speed of corrosion was measured in 3% H₂SO₄ solution at different temperatures. In case of 10% HNO₃ solution, the measurements were taken only at 20°C due to the quick deterioration of the sample.

According to metallographic studies the basic metal is exposed to corrosion in H₂SO₄ and H₃PO₄ solutions. The carbide-skeleton remains. In HNO₃ the selective solubility of the carbide component can be observed, so the speed of corrosion grows with the increase of TiC contents of the alloy.

The effect of some inhibitors that worked well in case of some carbon steels were examined as well in order to decrease the corrosion of TiC-Fe-Cr-Ni alloys, applying 0.5% inhibitor. In 10% HNO₃ solution thiocarbamide, in 3% H₂SO₄ and 44% H₃PO₄ PKU was used as inhibitor. (PKU = polycondensated product of urotropin, benzyl-chloride and aniline). The inhibitors substantially decrease the speed of corrosion. By temperature increase the protective effect slightly grows.

During our further work the corrosion- and wear-resistance of solid alloys (TiC-Fe-Cr) from titanium-carbide and chromium-steel in a powder-metallurgic way were studied in water with corrosion-abrasive, abrasive, gravimetric and electrochemical methods [22]. In the course of the experiments in the steel basic metal 33–60% TiC and 0–25% chromium-containing alloys were investigated. The corrosion- and wear-resistance of TiC-Fe-Cr alloys were studied in case of corrosion-abrasive and abrasive wear as a function of chromium- and TiC- contents. The corrosion-abrasive wear was measured in either water-containing 0.5% siliceous sand or 5% siliceous sand + 0.5% NaNO₂ inhibitor. Besides, the intensity of abrasion, in abrasive ray (siliceous sand) as well and also the speed of corrosion in water were investigated.

Protection of Steel-reinforcement by Inhibitors

The effectiveness of several inhibitors was studied in chloride-containing medium to protect steel-reinforcement of tight (cellular) concrete [23].

Nitrite, chromate, benzoate, phosphate salts and amine-derivatives were used as inhibitors. The investigations were carried out with carbon-steel sample-plate in wet-warm cell and in saturated Ca(OH)₂ + 2% CaCl₂-containing corrosive medium. It was found that the best results were achieved in case of the following inhibitor composition:

$\text{NaNO}_2 + \text{R}_2\text{NH}_2\text{NO}_2 +$ morpholine derivatives where R: cyclohexyl.

Chemical Agents Used for Salting Winter Roads

The corrosion-effect of chemical agents used for exemption the roads in winter of slipperiness was studied [24]. With laboratory examinations the corrosion processes going on in soil were studied. Instead of various soil tests the surface alteration on sample-plates was investigated and corrosion weight-loss was measured. During the experiments soils, sample plates and melting salts showed in *Table 1* were applied.

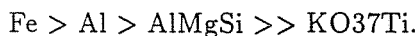
Table 1
Model-experiments in laboratory

Chemicals for thaw	Test plates	Soils
NaCl	Carbon steel	chernoz'om
MgCl ₂	(M2H)	
CaCl ₂	Aluminum	rendzina
CO(NH ₂) ₂	(Al 99.5)	
CaMg(CH ₃ COO) ₄	Aluminum-alloy	shifting sand
	(AlMgSi)	
	Corrosion resistant steel	
	(KO 37 Ti)	

Previously degreased and surface treated and weighed sample-plates put into different types of soils were sprayed with 10% solution of chemical agents 5 times a week throughout a month, then their weight-loss was determined. It was found that corrosion effect of the materials suitable for exemption of slipperiness decreases according to the following order:



The change of the deterioration of the structural material is as follows:



Among the types of soils the highest speed of corrosion was measured in the shifting sand, the results in case of rendzina and finally in that of chernoz'om were much better.

Finally, let us mention the education of postgraduate corrosion engineers also belongs to the work of the group of corrosion and electrochemical researches. The education has been regularly going on since 1964.

202 experts of this field received postgraduate degree. The students while preparing their diploma-work get into tight connection with the work of this special group. The co-operation is also active in helping the corrosion engineers with writing their MS thesis. Up to now at our Institute more than 40 MS theses have been prepared, which served the basis of several scientific lectures and publications.

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